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The Configuration and Formation of Percival Dianhydro-osazone

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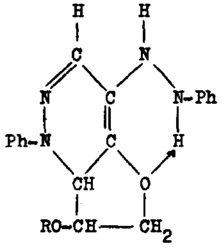
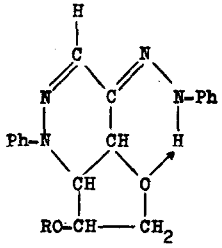
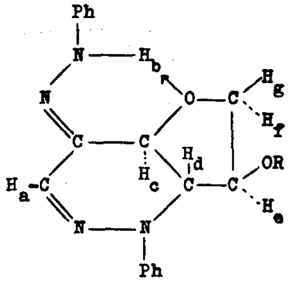
Henseke[1] suggested the tautomeric structures I and II for Percival dianhydro-osazone.



(I)



(II)



(III)

a, $R = H$; b, $R = CH_3CO$

We have studied the NMR spectrum of Percival dianhydro-osazone acetate (Fig. 1), and found that it possessed only one imino proton, thus favouring structure IIb. We therefore, excluded structure I which possesses two imino protons. The rest of the NMR spectrum was also in agreement with the carbon-hydrogen skeleton of IIb. The doublet at δ 5.08 ppm. was assigned to the

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[1] G. Henseke, U. Müller and G. Badicke, Chem. Ber., 91, 2270 (1958).

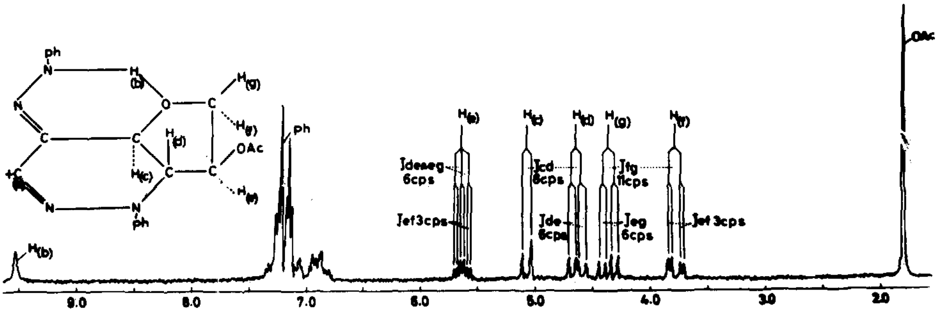

Fig. 1

methine proton of C-3 of the osazone precursor, which is linked to the etheric oxygen, it was coupled with a relatively large coupling (J= 8 cps.) to the proton whose resonance appeared at δ 4.65 ppm. which was assigned to the C-4 proton of the osazone precursor. This large coupling of J= 8 cps. was explained by an ax-ax trans relationship between C-3 and C-4 protons. The latter proton appearing at δ 4.65 ppm. was split by a large coupling of J= 8 cps. by the trans proton of C-3, and with a moderately large coupling of J= 6 cps. to the proton at about δ 5.65 ppm., assigned to the methine proton of C-5 bearing the O-acetyl group. The moderate size coupling of J= 6 cps. was also ascribed to a trans arrangement of the proton of C-4 and C-5 but probably quasi ax-ax. The proton of C-5 appearing at δ 5.65 ppm. was split with a coupling constant of J= 6 cps. by the trans proton of C-4 and the trans proton of C-6 methene, and a small coupling of J= 3 cps. by the cis proton at C-6. The geminal protons of the methene group at C-6 of the osazone precursor appeared at δ 4.3 and 3.7 ppm. Both being split by a large geminal coupling of J= 11 cps. The trans proton at δ 4.3 ppm. was split by the C-5 proton with a spin-spin coupling constant of J= 6 cps. and the cis methene proton at δ 3.7 ppm. with a coupling constant of J= 3 cps.

From the above, it is seen that we have in Percival dianhydro-osazone a trans arrangement between the protons of the C-3 and C-4, and a trans arrangement between those of C-4 and C-5. Since it is known that Percival dianhydro-osazone possesses the same configuration at C-5 as the starting osazone[2], we can now determine the configuration of C-3 and C-4. Thus, if we represent the dianhydro-osazone sideway with the OAc group above the plane of the rings (D-configuration) and the C-5 hydrogen below the plane of the rings, then the proton of C-4 will be above the rings and that at C-3 below the plane of the rings (Formula III).

We have found that osazone acetates having a 3,6-anhydro-ring such as (IV and V) did not give Percival dianhydro-osazone, irrespective of the configuration of their 3,6-anhydro-ring, they were merely hydrolysed to the starting 3,6-anhydro-osazone. Similarly, N-acetyl-osazones such as N-acetyl-tetra-O-acetyl-D-*lyxo*-hexulose phenylosazone (VI) failed to give a dianhydro-osazone, probably because the difficultly hydrolysable N-acetyl group delayed the anhydride formation between the hydrazone residue and the hydroxyl group of C-4, which must apparently preceed the formation of 3,6-anhydro-ring. This would explain the failure of 3,6-anhydro-osazone to give a dianhydro-osazone .

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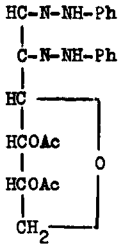
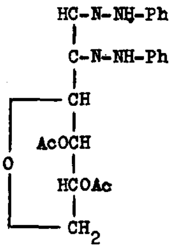
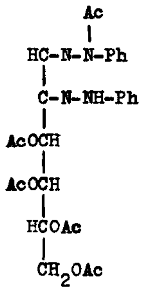
[2] E.G. Percival, *J. Chem. Soc.*, 1384 (1938).



(IV)



(V)



(VI)

We have also prepared a number of tetra-O-acetyl-*D*-*arabino*-hexulose arylosazones substituted in the phenyl ring with electron releasing groups, such as *o*-, *m*-, and *p*-CH_3, and *p*-OCH_3, and electron attracting groups, such as *p*-COOH and *p*-NO_2, and found that dianhydro-osazones could readily be obtained from the former osazone acetates but not the latter.